CORRELATION OF OSMOTIC PROPERTIES OF MEMBRANES WITH STRUCTURE

By

HAROLD GARTH SPENCER

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
August, 1959

ACKNOWLEDGMENTS

I am especially appreciative of the guidance given me by my faculty advisor, Dr. Charles E. Reid, the members of the supervisory committee and my fellow students.

I am also appreciative of the financial support of the Office of Saline Water, U.S. Department of the Interior, which made this investigation possible.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS ii

LIST OF TABLES iv

LIST OF FIGURES v

Chapter

I THE OSMOTIC PROCESS 1

II STRUCTURE AND OSMOTIC PROPERTIES OF MEMBRANES 4

- Procedures and Conventions
- Modification of PVA and Cellophane Membranes
- PVM/MA-PVA Membranes
- Evaluation of New Membranes
- Function of the Backing Membrane
- Durability of Membranes

III OHMIC RESISTANCE OF MEMBRANES 22

- Apparatus and Procedure
- Membrane Resistance to NaCl
- Membrane Resistance to Specific Ions
- Significance of Resistance Measurements

IV EFFECTS OF TESTING CONDITIONS ON THE OSMOTIC PROPERTIES OF PVM/MA-PVA MEMBRANES 33

- Effect of Temperature
- Effect of Pressure
- Effect of Concentration
- Discussion

V SUMMARY 39

BIBLIOGRAPHY 42

BIOGRAPHICAL NOTES 44

LIST OF TABLES

Table		Page
1.	Effect of membrane thickness on osmotic properties of PVM/MA-PVA membranes	10
2.	Osmotic properties of PVM/MA-PVA films cast on cellophane	13
3.	Effect of casting PVM/MA-PVA films on swollen cellophane	13
4.	Effect of thickness on the osmotic properties of PVM/MA-PVA films, carboxyl fraction of 0.50, cast on cellophane	15
5.	Osmotic properties of various membranes	16
6.	Osmotic properties of PVMK films cast on swollen cellophane	19
7.	Osmotic properties of membranes as a function of time	20
8.	Effect of temperature on the osmotic properties of a PVM/MA-PVA membrane cast on cellophane	34
9.	Effect of solution concentration on the osmotic properties of PVM/MA-PVA membranes	36

LIST OF FIGURES

Figure		Page
1.	Effect of baking time on the elongation of PVM/MA-PVA membranes of various carboxyl fractions.	9
2.	Effect of baking time on the osmotic properties of PVM/MA-PVA membranes of various carboxyl group fractions.	11
3.	Osmotic properties versus baking time for PVM/MA-PVA films cast on cellophane.	14
4.	Membrane resistance versus pressure for membranes with resistance values less than 1 kilohm.	24
5.	Membrane resistance versus pressure for membranes with high resistance.	26
6.	Membrane resistance to Na+ and Cl⁻ for ion-excluding membranes.	27
7.	Membrane resistance to Na+ and Cl⁻ for PVM/MA-PVA membranes.	29
8.	Membrane resistance to Na+ and Cl⁻ for cellophane and formaldehyde-cellophane membranes.	30
9.	Effect of pressure on the osmotic properties of a PVM/MA-PVA membrane cast on cellophane.	35

CHAPTER I

THE OSMOTIC PROCESS

The increasing demand on the world's supply of fresh water has prompted investigations of a variety of methods for the conversion of saline waters. Among these methods is the osmotic or ultrafiltration process. In this process, ions are filtered from a salt solution by forcing it through a supported membrane by means of direct hydrostatic pressure. The membrane must be capable of blocking ions while allowing the passage of water. When the investigation of this process was initiated, no membrane was known to be capable of effectively filtering or rejecting ions of salt solutions as concentrated as sea water. Thus, the investigation has necessarily been focused on the preparation and mechanism of salt-rejecting membranes.

Reid and Breton (1) evaluated several membranes and found that cellulose acetate (CA) would reject ions satisfactorily. Low durability and flow rate prevented its use in demineralizing saline water. However, an investigation of the water and ion transport through CA indicated that it functioned as an ion-excluding membrane, that is, both cations and anions were rejected with nearly equal facility. Since no existing theory completely explained the mechanism, the following theory was proposed: Water is held to the CA chains by hydrogen bonds, forming a continuous, oriented network throughout the pores of the membrane. The water molecules pass from one bonding site to the next by an alignment-type diffusion, while the ions which do not fit into the bound water network can pass only as defects form in it. This network can only be established when the interchain distances are not too large. These interchain distances are maintained in CA by crystalline regions.

If this mechanism is correct, a polymer which effectively excludes ions must have the following properties: (a) There must be a high concentration of hydrophilic groups. (b) Excessive separation of the chains must be prevented. (c) It must be chemically stable in the presence of saline water for extended periods. (d) It must form membranes which have adequate strength and flexibility.

Kuppers (2) has added support to the theory by determining activation entropy values for the diffusion of water through CA and cellophane, a membrane which rejects only about 8 per cent of the ions of a 0.1 M NaCl solution. He concluded that "the water molecule is constrained to a state of high order as it is transported through the membranes under high pressure differentials, the greater order being associated with the cellulose acetate film."

Membranes composed of a network of fixed charges of one sign, ion-selective membranes, have also been proposed as filters for the osmotic process (3). Theoretically, a porous membrane which contains an excess fixed charge relative to the solution with which it is in contact, will contain only a low concentration of ions of like charge. The application of pressure will force water of lower salt concentration through the membrane since the flux of the ions of like charge will be low because of the low concentration, and the effluent must be neutral. Hence, by effectively excluding either anions or cations, an ion-selective membrane will block the passage of salt when pressure is applied. Thus, ion-selective membranes should be effective salt filters. However, it has been suggested that the central portions of large pores will act as internal short circuits, reducing the ion-rejecting ability (4).

Most of the ion-selective membranes which have been investigated show only a moderate salt-rejection, 0 to 35 per cent of 0.1 M NaCl solutions at pressures up to 50 atms (1, 4). However, McKelvey et al. (5) recently reported ultrafiltration of salt solutions through Nalfilm 2 (National Aluminate Corp., Chicago, Ill.), and Gregor (6) has used interpolymer membranes under the influence of counter-osmotic pressure for demineralizing sea water for survival kits. McKelvey et al. (4) have also investigated the salt rejection of Permaplex C-10 (United Water Softeners Ltd., London, England) and found about 30 per cent salt rejection at high pressures by thick membranes of low water permeability. It was suggested that the pore size must be reduced by high pressure in order to obtain this moderate rejection.

Since high salt rejection has been observed for only a limited number of membranes, the investigation reported in this dissertation was initiated to determine more completely the correlation between the osmotic properties of membranes and their structure. The method of investigation is primarily one of evaluating osmotic and ohmic resistance properties of various membranes of different structure.

CHAPTER II

STRUCTURE AND OSMOTIC PROPERTIES OF MEMBRANES

It was apparent from the previous investigations that salt rejection by a membrane depends upon its fine structure as well as the nature of the functional groups present. The theories for ion-excluding and ion-selective membranes both indicate that the interchain distance must be restricted in order to obtain high salt rejection. If this is correct, it should be possible to obtain high salt rejection by sufficiently restricting the interchain distances of porous membranes containing either hydrophilic or exchange groups.

Reid and Breton (1) reported that polyvinyl alcohol (PVA) and cellophane have low salt rejection and high flow rates. Ohmic resistance measurements indicated that the salt rejection of cellophane would be significantly higher if high pressures were applied to restrict the interchain distances. This was found to be correct for both PVA and cellophane (7). Kuppers (2) found that the salt rejection of cellophane increased from 8 to 18 per cent when cross-linked with cupric ion. Thus, two approaches were followed in an attempt to obtain suitable membranes for this investigation: Modifications of PVA and cellophane were performed in an effort to obtain the necessary cross-linking. In addition, polymers which had not been previously tested were evaluated. The choice of these new polymers was based on the listed requirements for ion-excluding membranes.

Procedures and Conventions

The membranes were prepared by casting polymer solutions on a level glass sheet enclosed in a dry box. The thickness, which was measured with a dial indicator with an accuracy of ± 2 microns, was controlled by using a doctor blade and fixed concentrations. Membranes cast from aqueous solutions were stripped from the glass, but those cast from organic solvents were usually picked up on a wet paper towel. The treatments used to alter the fine structure of membranes were usually applied after their removal from the glass.

Membranes were also prepared by casting polymer solutions on cellophane taped to the glass casting sheet. It was necessary to dip the cellophane into the solvent used in the casting solution and then tape it to the glass immediately in order to obtain a flat surface upon which to cast. Several membranes were cast on swollen cellophane. In this procedure the plasticizer was removed from the cellophane by soaking in water for 3 weeks, changing the water frequently. The cellophane was then taped securely to the glass and maintained in a swollen condition. Films cast from aqueous solutions were cast on the wet cellophane and the composite membranes allowed to dry. When casting from acetone solutions the cellophane was allowed to dry in the swollen condition. before casting the film. It was possible to estimate the thickness of these films since the composition of the casting solution and the thickness of the layer spread by the doctor blade were known. Also, the increase in thickness of the composite membrane over that of cellophane alone was determined by the dial indicator.

An apparatus similar to the one described by Reid and Breton (1) was used to determine the osmotic properties of the membranes. It is briefly described as six membrane-supporting units in parallel, in which the membranes were clamped over porous supporting discs, connected to a solution reservoir, to which pressure was applied by means of compressed air. The solution was circulated across the membranes by convection.

The osmotic properties, salt rejection and flow rate, were evaluated at room temperature and at an applied pressure of 40 atms. Salt rejection was calculated as the per cent reduction in concentration of the influent 0.1 M NaCl solution, determined by comparing the conductivity of the effluent and reservoir solutions. The Mohr chloride analysis was used occasionally as a check determination. Flow rates were calculated as the microliters of effluent collected per hour through each square centimeter of membrane surface ($\mu l/hr/cm^2$).

Modification of PVA and Cellophane Membranes

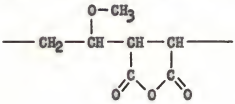
Flexible, insoluble PVA membranes about 15 microns thick were prepared by baking membranes cast from aqueous solutions of du Pont Elvanol, 72-60. Several modifications were performed. Variation of the baking time and temperature, stretching, treatment with formaldehyde, and aging in water vapor of high relative humidity gave no significant increase in salt rejection. Flow rates up to 500 $\mu l/hr/cm^2$ accompanied by less than 15 per cent salt rejection were observed. However, a significant improvement in the salt rejection was obtained by adding a small amount of PVM/MA, a 1-1 copolymer of methyl vinyl ether and maleic anhydride. The initial trials gave a salt rejection of about 40 per cent and flow rates of about 150 μl/hr/cm^2.

In an attempt to modify cellophane a procedure for reacting formaldehyde with viscose rayon (8) was followed. Cellophane membranes (du Pont PT-300, 22 microns thick) from which the plasticizer had been removed were soaked for one hour in a 15 per cent aqueous solution of formaldehyde containing a trace of NH_4Cl as a catalyst and then baked at 110-120°C. for 30 minutes. This treatment increased the salt rejection from 8 to about 45 per cent; however, the very favorable flow rate, about 500 μl/hr/cm^2, was reduced to about 20 μl/hr/cm^2. Kuppers (2) also observed a large reduction in flow rate when cellophane was cross-linked with cupric ion.

Further modifications of cellophane were not pursued because the flow rate was reduced so drastically. However, the investigation of PVM/MA-PVA membranes was extended to determine the effect of structural changes on their osmotic properties. This appeared feasible because the extent of baking and the ratio of PVM/MA to PVA could be readily controlled and both had an observable effect on the osmotic properties.

PVM/MA-PVA Membranes

PVM/MA, provided by the General Aniline and Film Corporation, is a linear polymer composed of the repeating unit (9):



It is water soluble and compatible with PVA which permits one to cast mixtures of the two from aqueous solutions. Flexible, insoluble membranes were prepared by moderate baking of mixtures containing small fractions of PVM/MA. Extended baking produced membranes too brittle for testing, but the discoloring observed with prolonged baking of PVA did not occur. Membranes containing carboxyl fractions (ratio of carboxyl groups to carboxyl plus hydroxyl groups) greater than about 0.09 were usually too brittle for testing, even with only moderate baking. However, a few tests were accomplished on membranes with a carboxyl fraction of 0.18. Apparently, only a moderate degree of cross-linking by esterification can be tolerated when flexible membranes are required.

An indication of the effect of baking time and carboxyl fraction on the fine structure of PVM/MA-PVA membranes was obtained by investigating their swelling properties when immersed in water. Weight increase and elongation for membranes baked for various periods of time were determined after immersing them in water at 30 ± 1°C. for 48 hours. This was sufficient time for the elongation to become constant. The blotting and weighing technique described by Priest (10) gave scattered results for the weight increase, but it became smaller as the baking period was increased. Successive measurements of the elongation of a particular membrane did not vary more than ± 1 per cent elongation. Elongation measurements for membranes of various carboxyl fractions as a function of the baking time are presented in Fig. 1. When compared after 5 hours of baking, elongation was reduced to 50 per cent of the value of PVA alone by the addition of a small amount of PVM/MA. Elongation decreased with increased baking time and carboxyl fraction, with

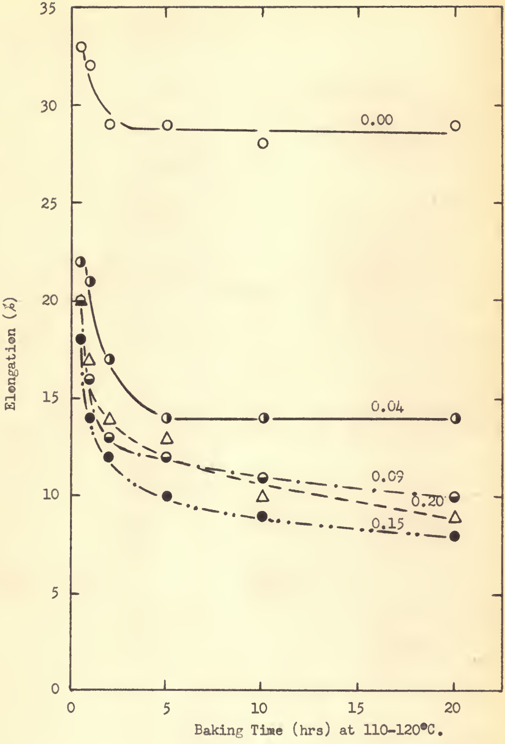


Fig. 1.--Effect of baking time on the elongation of PVM/MA-PVA membranes of various carboxyl fractions.

the exception of the 0.20 membranes. It is evident that cross-linking greatly reduced the swelling of these membranes and, hence, their interchain distances.

The changes in osmotic properties as a function of baking time and carboxyl fraction were determined (Fig. 2). Salt rejection increased as the baking time was extended and as the carboxyl fraction was increased. Flow rate was inversely related to the salt rejection. A comparison of these results with the swelling properties shows that salt rejection increased and flow rate decreased as the swelling was reduced.

The thickness of these membranes affected the flow rate to a much larger degree than the salt rejection (Table 1). The salt rejection was essentially the same for a membrane 28 microns thick as for one half as thick, while the flow rate was nearly 6 times as great in the thinner membrane as in the thicker one. The salt rejection did decrease for a very thin membrane, where defects would be more serious.

Table 1.-- Effect of membrane thickness on osmotic properties of PVM/MA-PVA membranes

Thickness (microns)	Flow Rate (μl/hr/cm^2)	Salt Rejection (%)
8	41	52
15	29	63
23	7	68
28	5	66

The highest salt rejection obtained for PVM/MA-PVA membranes was 82

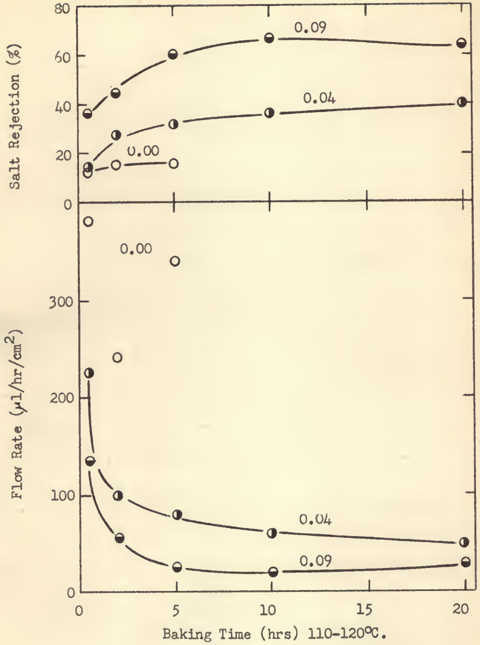


Fig. 2.--Effect of baking time on the osmotic properties of PVM/MA-PVA membranes of various carboxyl group fractions.

per cent for a membrane about 20 microns thick. The flow rate was only 4 μl/hr/cm^2.

Thin films containing high concentrations of PVM/MA were flexible enough to be tested if cast on cellophane. With low baking time, the films separated from the cellophane when tested. This resulted in high flow rates and low salt rejection. A longer baking time bonded the film to the cellophane and high rejection with reduced flow rates resulted (Table 2). The PVM/MA-PVA films swelled to a greater extent than cellophane, as indicated by the curling when immersed in water and by the swollen appearance of the film when not strongly bonded to the cellophane. Swelling was restricted by bonding to the cellophane, presumably by ester links, and a high salt rejection was obtained.

Salt rejection increased with baking time for a very thin film, about 4 microns, until it reached 98 per cent after 8 hours at 120-130°C. (Fig. 3). The salt rejection was inversely related to the flow rate.

The extremely low flow rates for membranes exhibiting high salt rejection were increased substantially, with some reduction in salt rejection, by casting on swollen cellophane (Table 3).

The relation between the osmotic properties of PVM/MA-PVA films with thickness is complicated by the requirement that they must bond to the cellophane to produce high salt rejection. Thick membranes were brittle and tended to swell and separate from the cellophane in the presence of water. Thus, films of intermediate thickness gave higher salt rejection and lower flow rates than very thin or very thick films (Table 4).

Table 2.-- Osmotic properties of PVM/MA-PVA films cast on cellophane

Carboxyl Fraction	Flow Rate (μl/hr/cm^2)	Salt Rejection (%)	Separation from Cellophane
Baked 2 hours at 100-110°C.			
0.33	64	68	No
0.50	200	15	Yes
0.67	200	16	Yes
1.00	320	10	No
Baked 19 hours at 100-110°C.			
0.00	205	13	No
0.33	13	90	No
0.50	22	92	No
0.67	19	79	No
1.00	61	31	No

Table 3.-- Effect of casting PVM/MA-PVA films on swollen cellophane*

Cast on Cellophane		Cast on Swollen Cellophane	
Flow Rate (μl/hr/cm^2)	Salt Rejection (%)	Flow Rate (μl/hr/cm^2)	Salt Rejection (%)
9	98	91	86
		84	90

*Films were approximately 4 microns thick, and were baked for 8 hours at 120-130°C.

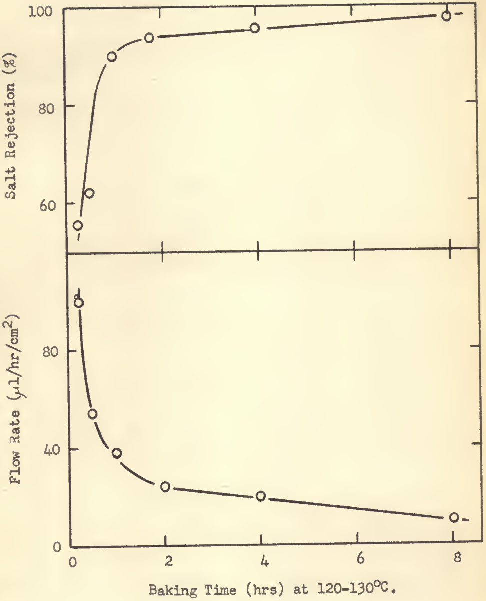


Fig. 3.--Osmotic properties versus baking time for PVM/MA-PVA films cast on cellophane.

Table 4.-- Effect of thickness on the osmotic properties of PVM/MA-PVA films, carboxyl fraction of 0.50, cast on cellophane

*Thickness (microns)	Flow Rate ($\mu l/hr/cm^2$)	Salt Rejection (%)
1	17	78
4	10	94
8	14	71
20	190	15

*The thickest film was cast from a solution calculated to produce a membrane approximately 20 microns thick. The remaining membranes were prepared from diluted solutions of the original casting solution.

This investigation of structure and osmotic properties has demonstrated that PVM/MA-PVA membranes possessing high salt rejection can be prepared. The high salt rejection depends on high concentrations of PVM/MA and on the restriction of interchain distances by cross-linking within the membrane and by bonding to cellophane.

Evaluation of New Membranes

Several membranes containing hydrophilic groups were prepared and their osmotic properties evaluated. Table 5 lists the results of these tests. Three of these membranes, cellulose isobutyrate, polyvinyl methyl ketone (PVMK) cast on cellophane and polyvinyl acetate (PVAc) cast on cellophane, exhibited moderately high salt rejection. All three were cast from acetone solutions. The composite membranes composed of PVMK on cellophane and PVAc on cellophane were placed in the apparatus with the cellophane on the downstream side. The change in the osmotic properties of PVMK and PVAc caused by the presence of the cellophane backing membrane prompted a consideration of its function which is presented in the next section.

Table 5.-- Osmotic properties of various membranes

Membrane	Flow Rate (μl/hr/cm^2)	Salt Rejection (%)	Remarks
Cellulose isobutyrate (Tenn. Eastman Co.)	40	87	Failed rapidly.
*Cellulose acetate butyrate (Tenn. Eastman Co.)	10	8	
Mylar C (du Pont Co.)	10	0	Flow rate increased during run.
Nylon-6 (Chemstrand Corp.)	52	15	Flow rate decreased during run.
PVMK	35	3	
PVMK on cellophane	40	60	
PVAc	66	0	Reported previously at 70 atms (7).
PVAc on cellophane	4	70	

*Also reported by Reid and Breton (1).

The PVMK polymer was prepared from methyl vinyl ketone (Chas. Pfizer & Co., Inc.) by the bulk polymerization method outlined by Marvel and Levesque (11). Vinyl acetate (Matheson Coleman and Bell, Inc.) was polymerized by an emulsion polymerization method (12). The Nylon-6 membranes cast from commercial formic acid solutions were cloudy. This cloudiness may be caused by occlusion of the solvent and perhaps the osmotic properties listed in Table 5 for Nylon-6 differ from the values that would have been obtained if clear membranes had been prepared. When cresol or hot phenol was used as solvent, the membranes were also cloudy; however, the flow rates were too rapid to permit evaluation.

Function of the Backing Membrane

Properties of several membranes have been altered significantly by backing or supporting them with cellophane. It has been shown that the interchain distances of PVM/MA-PVA films cast on cellophane are restricted by chemical bonding of the film to the cellophane. PVMK and PVAc membranes are effective salt filters only when supported by cellophane. They would not be expected to bond chemically with cellophane; however, weaker adhesion forces would be present. McLaren (13) has investigated the adhesion of a large number of polymeric films to cellophane. He concludes that polymers cast from nonaqueous solutions penetrate cellophane very little and that the adhesion is functional group specific. Amorphous polymers with hydrogen bonding groups have a strong affinity for cellophane which is increased by the application of heat and pressure.

The osmotic properties of PVMK were investigated under various conditions to determine the function of the cellophane backing membrane. Several observations of the results of this investigation indicated that a weak interaction at the PVMK-cellophane interface was responsible for their salt rejection: The PVMK film was easily stripped from the cellophane when wet. Preformed membranes laid on cellophane also gave a moderately high salt rejection. In one case the salt rejection started low and increased during the run. Membranes of PVMK cast on cellophane tested in an inverted position, PVMK on the downstream side, behaved like cellophane alone.

In order to determine the effect of increasing the adhesion of PVMK to cellophane on the osmotic properties of this membrane, the heat and pressure suggested by McLaren (14) were applied to a sandwich of cellophane laid on PVMK cast on cellophane. Salt rejection was lower and flow rate higher for this membrane than for a membrane which had not been subjected to the heat and pressure treatment. The rejection did increase to equal that of the untreated membrane after about 10 days. A similar treatment of PVAc cast on cellophane also reduced its salt rejection and increased its flow rate. Apparently, the structure at the film-cellophane interface which is responsible for the salt rejection was not induced further by increasing the adhesion.

In another attempt to increase the interaction at the PVMK-cellophane interface, PVMK was cast on swollen cellophane. This procedure was expected to permit PVMK to penetrate into the pores of the cellophane to some extent. High salt rejection and low flow rates were observed for these membranes. Table 6 illustrates the increase in salt rejection and decrease in flow rate which resulted when PVMK was cast on swollen cellophane rather than on the usual cellophane.

It is apparent that the salt rejection by PVMK films cast on cellophane is a property of the interface between the two polymers. The structure in the interfacial region was not determined; however, the properties of PVMK and cellophane allow one to propose a description of the function of the two polymers which is consistent with the bound water mechanism. PVMK has a high concentration of hydrophilic groups, but the polymer is amorphous and not cross-linked. Thus, if the bound water theory describes the mechanism by which the composite membrane rejects salt, the apparent role of the backing membrane is to stabilize the interchain distances of the PVMK in the interfacial region. Perhaps the cellophane can be described as a supporting matrix for the PVMK polymer which has penetrated into its pores and thus stabilizes the interchain distances of the PVMK in this region.

Table 6.— Osmotic properties of PVMK films cast on swollen cellophane

On Cellophane		On Swollen Cellophane	
Flow Rate (μl/hr/cm^2)	Salt Rejection (%)	Flow Rate (μl/hr/cm^2)	Salt Rejection (%)
46	52	13	85
40	58	9	94

Another description which seems possible is that the penetration of PVMK into the pores essentially reduces the pore sizes of the cellophane in the interfacial region which would increase its salt rejection. However, this does not seem likely because it has previously been shown that even at pressures as high as 340 atms cellophane, which is easily compressed, rejects only about 40 per cent of the ions (7). Also, the salt rejection was only 13 per cent when PVA was cast on cellophane and only 31 per cent when PVM/MA was cast on cellophane and the composite membrane baked to enhance cross-linking (Table 2).

Durability of Membranes

The osmotic properties of a few membranes were tested for several weeks in order to obtain an estimate of their durability. The results are tabulated in Table 7. None of the membranes failed abruptly. The durability of the PVM/MA-PVA membrane cast on cellophane was good. Despite the presence of ester groups, it was much more durable than the cellulosic esters. One explanation is that the cross-linking prevents the swelling that preceeds hydrolysis in CA (1). In addition, the ester group may be less susceptible to hydrolysis because of steric effects since it is a link between two large multi-linked polymer molecules. Flow rate and salt rejection of PVMK membranes usually increased as the test progressed.

Table 7.— Osmotic properties of membranes as a function of time

Membrane	Duration of Test (weeks)	Initial		Change	
		Flow Rate $(\mu l/hr/cm^2)$	Salt Rejection (%)	Flow Rate $(\mu l/hr/cm^2)$	Salt Rejection (%)
PVM/MA-PVA on cellophane	25	23	92.5	0	-1.3
PVM/MA-PVA (0.18)	13	127	44	41	-7
PVMK on cellophane	8	50	90.0	35	2.5
Cellulose isobutyrate	3 days	40	87	148	-40

It appeared possible that the addition of a small amount of PVM/MA to CA might cross-link with the residual hydroxyl groups of CA when baked which would prevent its swelling and subsequent hydrolysis. This did not occur. The addition of 10 per cent PVM/MA to 39.4 per cent acetyl CA produced membranes which exhibited slightly lower initial salt rejection and failed more rapidly than when the PVM/MA was not included. It has also been shown that the use of succinyl chloride as the cross-linking agent does not increase the durability of CA (15).

CHAPTER III

OHMIC RESISTANCE OF MEMBRANES

Reid and Breton (1) related the resistance to transport of NaCl and of specific ions through CA and cellophane to ohmic resistance. The comparable resistance of CA to both Na+ and Cl^- indicated that it functioned as an ion-excluding membrane. Several observations supported the bound water theory: Membranes with high salt rejection had high resistance to NaCl. The resistance of CA to H+ was very low and did not increase with pressure. The resistance to NaCl of CA and cellophane increased with pressure. The results were interpreted to indicate that the water was transported by a different mechanism from the ions.

Similar measurements were carried out on the membranes included in this investigation to determine whether the membranes were ion-selective or ion-excluding and whether or not the properties of the ion-excluding membranes were consistent with the bound water theory.

Apparatus and Procedure

The apparatus differed from the one described by Reid and Breton (1) in that the contact surfaces of the whetstone compressing blocks were square instead of circular and had an area of 1.0 cm^2 instead of 1.41 cm^2. Thus, the resistance values reported are for membranes 1.0 cm^2 in area. Also, both electrodes, instead of just the cathode, were silver, silver chloride. Runs were made at room temperature using a direct current of less than 0.5 microamperes. The whetstone blocks were soaked in a 0.018 M NaCl or HCl solution prior to each run. The membranes were prepared by soaking them in water and blotting several times with filter paper. The resistance of the cell without the membrane was first determined over the pressure range, then the membrane was inserted and the resistance measured again. Membrane resistance was calculated as the difference between the two measurements. Readings were made after 2 minutes at the desired pressure.

The membrane resistance to NaCl was determined as the pressure was raised to a maximum and then reduced. The results varied unless the membranes were inserted between filter papers which had been soaked in the salt solution.

The membrane resistance to H^+, Na^+ and Cl^- were determined by sandwiching the membranes between either Amberplex cation or anion exchange membranes in the desired form. The resistance of the exchange membranes was first determined and was found to be nearly constant over the pressure range. Then the membrane was inserted, the pressure raised to about 250 atms and the resistance determined as the pressure was reduced.

Membrane Resistance to NaCl

Resistances of cellophane, formaldehyde-cellophane, PVA and PVM/MA-PVA membranes were less than 1 kilohm. The resistances increased with pressure, as is shown by some typical runs presented in Fig. 4. Results for a particular membrane varied but the shape of the curve and its range, less than 1 kilohm, were consistent. The accuracy was

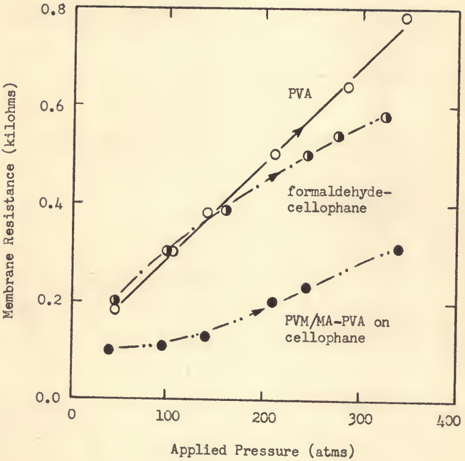


Fig. 4.—Membrane resistance versus pressure for membranes with resistance values less than 1 kilohm.

limited because a membrane resistance of 0.1 kilohm corresponds to an increase of only 3 to 4 per cent of the cell resistance without the membrane.

Cellulose isobutyrate, CA, PVMK on cellophane, and PVAc on cellophane had resistances of the order of 10 to 100 kilohms and these resistances increased with pressure (Fig. 5). Cellulose acetate butyrate had a resistance of about 1,000 kilohms, and Mylar was much higher. The resistance of PVMK not cast on cellophane increased rapidly with time under constant pressure, so the variation of the resistance with pressure was not determined.

If the differences in thickness, crystallinity and porosity are not great, high resistance is expected to accompany high salt rejection for membranes functioning as ion-excluding membranes. The exceptions to this expected behavior were PVM/MA-PVA membranes, which had low resistance but high salt rejection, and the membranes which had no salt rejection: cellulose acetate butyrate, Mylar and PVMK.

Membrane Resistance to Specific Ions

Cellulose isobutyrate, PVMK on cellophane and PVAc on cellophane had resistances to Na+ and Cl⁻ which indicated that they function as ion-excluding membranes (Fig. 6). The resistance to H+ by cellulose isobutyrate and PVMK on cellophane was less than 10 per cent of their resistance to NaCl and Na+, which is consistent with the results for CA. Thus, their resistance properties are consistent with the bound water mechanism. The resistance of PVAc on cellophane to H+ was about the same as for NaCl or Na+; however, this membrane had a very low flow rate

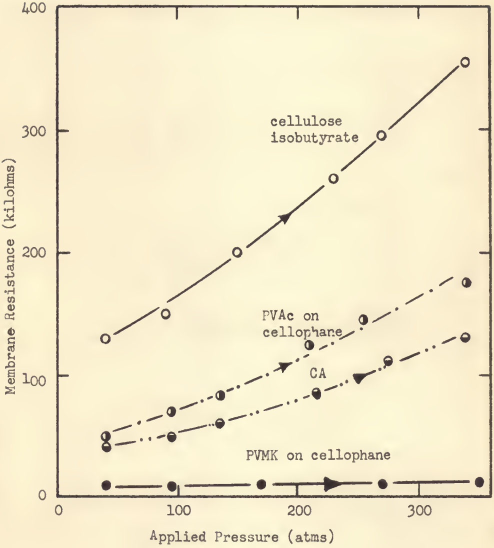
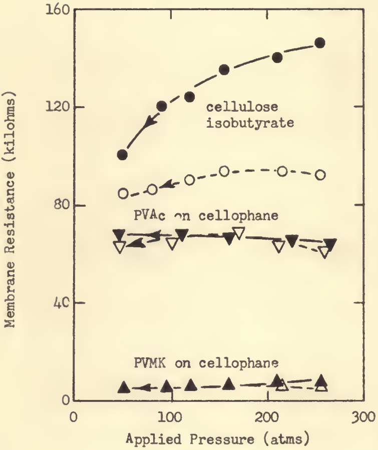


Fig. 5.--Membrane resistance versus pressure for membranes with high resistance.



Open symbols: Resistance to Cl^-
Solid symbols: Resistance to Na^+

Fig. 6.—Membrane resistance to Na^+ and Cl^- for ion-excluding membranes.

which may account for its high resistance to H+.

PVM/MA-PVA membranes exhibited much higher resistance to Cl^- than to Na+, which indicated that they function as ion-selective membranes. The resistance of PVA to Na+ and Cl^- was approximately the same, but the resistance to Cl^- increased to possibly 20 times the resistance to Na+ for a PVM/MA-PVA membrane, of carboxyl fraction 0.50, cast on cellophane (Fig. 7). A similar membrane was tested after removing it from the osmotic property testing apparatus. It was washed and soaked in 0.018 M NaCl prior to testing. The membrane rejected 88 per cent of the ions and its resistance to Cl^- was about 9 times its resistance to Na+. Gregor and Wetstone (16) have investigated various electrical properties of interpolymer membranes composed of PVM/MA and Dynel, an inert matrix used to support the polyelectrolyte, and found them to be highly selective.

Apparently only a small fraction of the carboxyl groups are used in cross-linking the membrane, leaving the greater portion to act as exchange sites. Additional evidence for this hypothesis was obtained from the infrared spectra of PVM/MA-PVA membranes taken after various periods of baking. Absorption at 1860 cm^{-1} and 1785 cm^{-1}, characteristic of anhydride groups (17) of membranes baked for a short period of time, did not diminish significantly with extended baking.

Fig. 8 shows that the selectivity of cellophane increased when it was cross-linked with formaldehyde. Salt rejection by cellophane of salt solution of low concentration has been attributed to its selectivity, with the hydroxyl groups acting as exchange sites (1, 18). Apparently the pore sizes are reduced by cross-linking with formaldehyde,

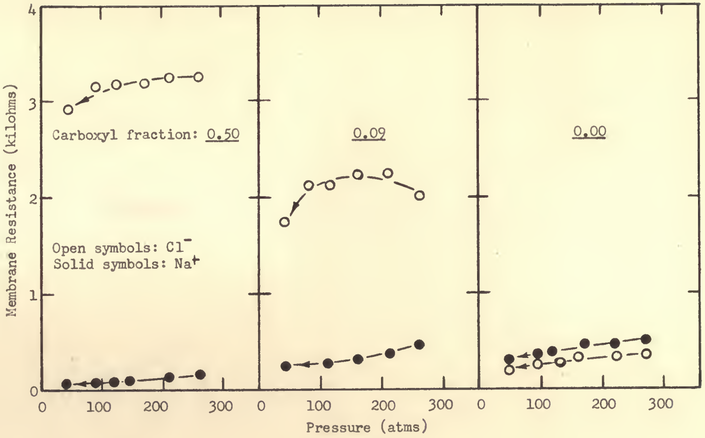


Fig. 7.—Membrane resistance to Na^+ and Cl^- for PVM/MA-PVA membranes.

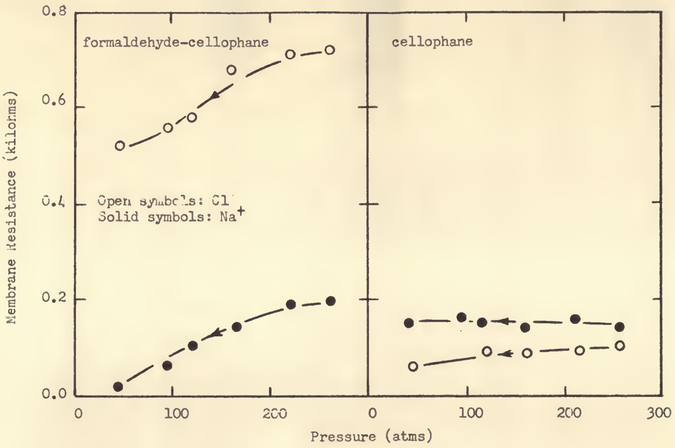


Fig. 8.—Membrane resistance to Na^+ and Cl^- for cellophane and formaldehyde-cellophane membranes.

as indicated by the much lower flow rate, so that the weak exchange sites can more easily protect the pores.

Significance of Resistance Measurements

The resistance measurements provided a means of differentiating ion-excluding membranes from ion-selective membranes. A significant result was the demonstration that high salt rejection by ion-excluding membranes is not restricted to membranes containing ester linkages. PVMK functioned as an ion-excluding membrane when cast on cellophane. In addition its resistance properties were consistent with the predictions of the bound water theory. The result that salt rejection was only obtained when the membrane was cast on cellophane supports the theory that high salt rejection by ion-excluding membranes depends on the restriction of the interchain distances. This was also supported by the osmotic properties of PVAc membranes.

A second significant result was the demonstration that PVM/MA-PVA membranes function primarily as ion-selective membranes. The bound water mechanism is not excluded, but the membranes' low resistance to NaCl implies that this mechanism plays only a minor role. It was demonstrated in the investigation of the structural and osmotic properties of these membranes that high salt rejection requires restriction of the interchain distances and a high concentration of carboxyl groups. The increase in salt rejection and the apparent increase in selectivity of cellophane caused by cross-linking it with formaldehyde also support the hypothesis that salt rejection depends on the restriction of the interchain distances as well as on the concentration of exchange groups.

The PVM/MA-PVA membranes demonstrate a method of preparing ion-selective membranes which has not been exploited. Homogeneous membranes are usually prepared by forming resins in sheet form, copolymerizing monomeric ionic compounds with cross-linking agents or treating inert membranes to produce the desired ionic groups (6). The homogeneous, interpolymer membranes investigated by Gregor (6) were prepared by casting mixtures of polybase or polyacid polymers with an inert membrane-forming polymer. PVM/MA-PVA membranes are interpolymer membranes, but have the added versatility of being readily cross-linked. The membranes can also be made very thin and supported by cellophane in order to make them strong and flexible. A private communication from General Aniline and Film Corporation indicates that PVM/MA cross-links with various polyalcohols to form insoluble materials. Hence, it is possible that a variety of polyacids and polyalcohols could be used to prepare ion-selective membranes by this method.

CHAPTER IV

EFFECTS OF TESTING CONDITIONS ON THE OSMOTIC PROPERTIES OF PVM/MA-PVA MEMBRANES

The effects of temperature, pressure and concentration on the osmotic properties of the ion-selective PVM/MA-PVA membranes were investigated.

Effect of Temperature

An apparatus with a single membrane-supporting unit was used to determine the effect of temperature on the osmotic properties. The temperature was controlled by enclosing the unit in a can of water through which was circulated water of the desired temperature. The water was also passed through the cooling jacket to preheat or precool the salt solution prior to its contact with the membrane. The temperatures recorded were those of the water surrounding the unit and were constant within ± 1°C.

An attempt to increase the salt rejection of a membrane of low PVM/MA content by lowering the temperature from 30 to 9°C. resulted in only a small increase, 52 to 60 per cent. However, the flow rate decreased sharply, 52 to 28 $\mu l/hr/cm^2$. This result suggested that the low flow rate of membranes of high salt rejection might be increased by raising the temperature while the salt rejection would not be reduced appreciably. The subsequent test showed that the flow rate was increased by 400 per cent by raising the temperature from 30 to 73°C. (Table 8).

The corresponding decrease in salt rejection was from 98 to 95 per cent. It should be noted that the membrane failed rapidly at 91°C.; however, no significant deterioration was observed when the temperature was maintained at 60 to 70°C. for 2 weeks.

Table 8.-- Effect of temperature on the osmotic properties of a PVM/MA-PVA membrane cast on cellophane

Temperature (°C.)	Flow Rate ($\mu l/hr/cm^2$)	Salt Rejection (%)
30	11	98
53	25	97
73	57	95
*91	91-130	92-82

*Rapid deterioration occurred at this temperature. The values reported are those at the beginning and end of 24 hours of testing.

Effect of Pressure

The osmotic properties of a PVM/MA-PVA film cast on cellophane were determined over the pressure range 7 to 55 atms and the results compared with the salt rejection of CA reported by Reid and Breton (1). The results are pictured in Fig. 9. The flow rate increased linearly with pressure over the range tested. High salt rejection was observed even at the low pressures and increased as the pressure was raised.

Effect of Concentration

The influent NaCl concentration was varied over the range 0.11 to

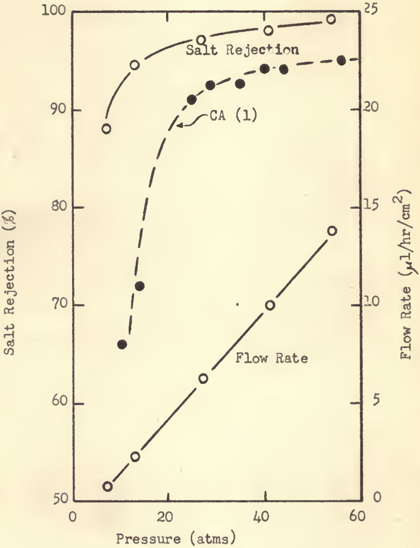


Fig. 9.--Effect of pressure on the osmotic properties of a PVM/MA-PVA membrane cast on cellophane.

0.57 *M*. An applied pressure of 30 atms in excess of the osmotic pressure of the solution was maintained. The results of this test are presented in Table 9. Under these conditions salt rejection and flow rate did not vary significantly for membranes of carboxyl fraction 0.50, cast on cellophane, which possessed high salt rejection. However, flow rate increased and salt rejection decreased at the high concentrations for a membrane of carboxyl fraction 0.09, not cast on cellophane, which had only a moderate salt rejection.

Table 9.— Effect of solution concentration on the osmotic properties of PVM/MA-PVA membranes

Concentration: (*M*, in order)	0.57	0.24	0.11	0.54
Carboxyl fraction, 0.50				
Flow rate:	24	26	24	26
Salt rejection:	87	90	91	87
Carboxyl fraction, 0.50				
Flow rate:	12	13	12	13
Salt rejection:	95	96	95	95
Carboxyl fraction, 0.09 (not on cellophane)				
Flow rate:		25	21	28
Salt rejection:		45	49	40

Flow rate given in units of μl/hr/cm^2, salt rejection in per cent.

Discussion

These results demonstrate that PVM/MA-PVA membranes are effective salt filters at concentrations comparable to that of sea water, and that their behavior at the usual testing concentration of 0.1 M NaCl is indicative of their behavior at higher concentrations. Sea water is composed of lesser concentrations of salts other than NaCl. Their effects on the durability and osmotic properties were not investigated. Gregor (6) indicated that complexing ions such as copper would decrease the selectivity of membranes containing carboxyl groups. However, the osmotic properties of a PVM/MA-PVA membrane soaked overnight in a 0.1 M $CuSO_4$ solution were not affected.

It has also been demonstrated that the flow rate can be increased by increasing either the pressure or the operating temperature. It should be mentioned, however, that even with this increase the membranes as presently prepared fall short of the desired flow rates for use in demineralizing sea water.

The increase in the flow rate of an ion-selective membrane with pressure is contrary to results of other investigators. McKelvey (4) reported that flow rates decreased with increased pressure for a Permaplex C-10 membrane. The fine structure of PVM/MA-PVA membranes is apparently stable enough to inhibit large reductions in interchain distances so that the flow rate increased as the pressure differential was increased. However, there must be some increase in the restriction of the interchain distances to cause the increase in salt rejection. Gregor (6) has indicated that the flow rate at 50 atms for interpolymer ion-selective membranes is an order of magnitude lower if the stress is applied by direct hydrostatic pressure than if the same stress is applied by counter-osmotic pressure. This phenomenon was attributed to the compression of the film under the hydrostatic pressure.

CHAPTER V

SUMMARY

The osmotic and ohmic resistance properties of several membranes were determined and correlated with their structures. The resistance properties provide a means of classifying the membranes. Membranes with high resistance to NaCl, Na^+ and Cl^- are ion-excluding membranes. Those with low resistance to NaCl and Na^+, but high resistance to Cl^- are ion-selective membranes. The results of the investigation of the several membranes are summarized below:

The low salt rejection of cellophane and polyvinyl alcohol is increased by cross-linking. The flow rate is reduced by this treatment. Polyvinyl alcohol is readily cross-linked by baking a mixture containing a small amount of a 1-1 copolymer of methyl vinyl ether and maleic anhydride. Cellophane is cross-linked by baking a membrane containing formaldehyde. Both membranes function as ion-selective membranes. Apparently the addition of carboxyl groups to the polyvinyl alcohol and the restriction of its swelling by cross-linking are responsible for the increase in salt rejection. Excessive baking or high concentrations of the polymeric anhydride produce membranes which are too brittle or not strong enough for determining the osmotic properties. Thus, only moderately high salt rejection can be obtained for these membranes.

Strong, flexible membranes capable of high salt rejection are obtained when films containing large fractions of the polymeric anhydride are cast on cellophane. Swelling of these films is restricted by bonding to the cellophane supporting membrane. The durability of these membranes is good. The low flow rate can be increased by casting the films on swollen cellophane, by raising the pressure or by increasing the temperature.

Cellulose isobutyrate membranes have high salt rejection and low flow rates, fail rapidly and function as ion-excluding membranes. Their properties are consistent with the bound water mechanism.

Membranes composed of polyvinyl methyl ketone and polyvinyl acetate do not reject salt; however, a moderately high salt rejection is observed when thin films of these polymers are backed by untreated cellophane. Apparently the salt rejection is the result of greater stabilization of the interchain distances in the interfacial region by the backing membrane. Both membranes function as ion-excluding membranes. High salt rejection by polyvinyl methyl ketone is obtained when the adhesion is increased by casting the polymer on swollen cellophane. The high salt rejection by this membrane containing carbonyl groups is significant because it demonstrates that high salt rejection by ion-excluding membranes is not ester linkage specific.

The properties of the ion-excluding membranes are consistent with the bound water mechanism. The properties of the ion-selective membranes are consistent with the theory that a high concentration of fixed charges are required to restrain the ions. The salt rejection for either type of membrane depends on a high concentration of the required functional groups and restricted interchain distances. Salt rejection is inversely related to the flow rate. Thus, despite their different mechanisms each type of membrane is essentially a filter and the smaller the pores the more effective the filter and the lower the flow rate.

BIBLIOGRAPHY

(1) C. E. Reid and E. J. Breton, J. Appl. Polymer Sci., 1, 133-43 (1959).

(2) J. R. Kuppers, "Physical Characteristics of Osmotic Membranes of Organic Polymers," Ph.D. Dissertation, Department of Chemistry, University of Florida, August, 1957.

(3) C. B. Ellis, "Fresh Water from the Ocean," The Ronald Press Co., New York, 1954.

(4) J. G. McKelvey, K. S. Spiegler and M. R. J. Wyllie, J. Phys. Chem., 61, 174-8 (1957).

(5) J. G. McKelvey, K. S. Spiegler and M. R. J. Wyllie, paper presented at A. I. Ch. E. Symposium on Adsorption, Dialysis and Ion Exchange, Baltimore, 1957; through proceedings of a symposium, "Saline Water Conversion," National Academy of Sciences and National Research Council, Publication 568, Washington, D. C., 1957.

(6) Proceedings of a symposium, "Saline Water Conversion," National Academy of Sciences and National Research Council, Publication 568, Washington, D. C., 1957.

(7) H. G. Spencer, "Osmotic Characteristics of Some Polymeric Organic Membranes at High Pressures," M.S. Thesis, Department of Chemistry, University of Florida, February, 1958.

(8) E. M. Kärrholm, Textile Research J., 25, 756-62 (1955).

(9) General Aniline and Film Corp., "New Product Bulletin No. P-103," New York.

(10) W. J. Priest, J. Polymer Sci., 6, 699-710 (1951).

(11) C. S. Marvel and C. L. Levesque, J. Am. Chem. Soc., 60, 280-4 (1938).

(12) G. F. D'Alelio, "A Laboratory Manual of Plastics and Resins," J. Wiley and Sons, Inc., New York, 1943.

(13) A. D. McLaren, Modern Plastics, 31, No. 11, 114-6, 181 (July, 1954).

(14) A. D. McLaren, J. Polymer Sci., 3, 652-62 (1948).

(15) "Development of Synthetic Osmotic Membranes for Demineralization of Sea and Other Saline Waters," Unpublished Progress Report No. 10, U.S. Department of the Interior, Contract No. 14-01-001-71, July 31, 1956.

(16) H. P. Gregor and D. M. Wetstone, J. Phys. Chem., 61, 147-51 (1957).

(17) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1954.

(18) J. W. McBain and R. F. Stuewer, J. Phys. Chem., 40, 1157-68 (1936).

BIOGRAPHICAL NOTES

Harold Garth Spencer was born May 19, 1930, in Avon Park, Florida. He attended elementary and secondary schools in the same city. He entered the University of Florida in 1948, and received his B.S. degree in Education in 1952. Following two years' active duty with the U.S. Air Force and one year as teacher in the Avon Park High School, he again enrolled at the University of Florida. He received his M.S. degree, with a major in chemistry and a minor in mathematics, in February, 1958. Since his return to the University of Florida, he has held the positions of graduate assistant, teaching assistant and research assistant with the Saline Water Project. He is a member of Kappa Kappa Psi, Kappa Delta Pi and Phi Kappa Phi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 8, 1959

Dean, College of Arts and Sciences

Dean, Graduate School

SUPERVISORY COMMITTEE:

C. E. Reid
Chairman

W S Bray
Co-Chairman

G E Ryschkewitsch